Hydrogen Bonding in Polyamide Toughened Novolac Type Phenolic Resin

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ABSTRACT: The hydrogen bonding, miscibility, and thermal stability of polyamide toughened novolac type phenolic resin were investigated. The intermolecular force of the resin increased with the content of the soft segments of polyamides (nylon 6, nylon 66) that absorb the loads in the network of brittle phenolic resin. IR (IR region) spectra and differential scanning calorimetry results confirmed that the phenolic/polyamide blend was completely miscible. Its thermal degradation temperature was higher than 400°C and increased with the increasing of polyamide content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2283–2289, 1999

Key words: novolac type phenolic resin; polyamide; intermolecular hydrogen bonding; thermal stability

INTRODUCTION

Phenolic resins have been widely used as paints, adhesives, and other products because of their excellent flame resistance, dimensional stability, and chemical resistance.[1–3] In recent years much emphasis has been placed on fireproof structures and decorations for public security in buildings; phenolic resin is one of the most popular resins for this purpose. However, its brittleness has significantly limited its application. The improvement of the toughness of phenolic resin is an important task for further applications.[4–7] One method of modifying phenolic resin is to blend it with other miscible thermoplastic polymers. As described in our previous articles,[3,8–14] phenolic resin provides intermolecular hydrogen bonding as a dominant driving force of interaction with the hydroxyl, carbonyl, amide, and ester groups and other hydrogen bonding containing functional groups of miscible thermoplastic polymers. The physical properties of modified phenolic resin are increased with the addition of thermoplastic modifier, because either ester or other hydrogen bonding functional groups are better than phenolic resin in absorbing the load.

The fit of the glass transition temperature (T_g) from the differential scanning calorimetry (DSC) with the predictions from the Fox,[12] Gordon–Taylor,[11] and Kwei[9] equations[12–14] was studied. The hydrogen bonding in the blending of the novolac type phenolic resin with polyamide was investigated.

In this study a novel method of blending a novolac type phenolic resin with polyamide is proposed to improve the physical properties of the phenolic. The interaction of the amide group of polyamide (nylon 6, nylon 66) with hydrogen bonding of the phenolic resin was studied. The miscibility and thermal stability of a phenolic/polyamide blend were investigated.
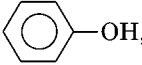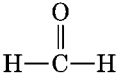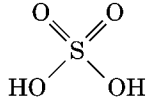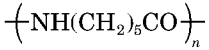
EXPERIMENTAL

Materials

The synthetic method and the analytical technique for novolac type phenolic resin were de-

Table I Materials Used in Study

No.	Reagent	Structure	Supplier
1	Phenol	⬡—OH, $M_w = 94.11$, purity $> 98.0\%$	Union Chemical Works Ltd., Taiwan
2	Formaline	$H-\overset{\overset{\textstyle O}{\|}}{C}-H$ 37 wt % water solution	Union Chemical Works Ltd., Taiwan
3	Concn sulfuric acid	$HO-\overset{\overset{\textstyle O\diagdown\diagup O}{S}}{}-OH$ $M_w = 190.21$, purity $> 96.0\%$	Hayashi Pure Chemical Industries Ltd., Japan
4	Nylon 6	$+NH(CH_2)_5CO+_n$	Taiwan Chemical Co., Taiwan
5	Nylon 66	$+NH(CH_2)_6NHCO(CH_2)_4CO+_n$ Dupont 101L	DuPont Co.

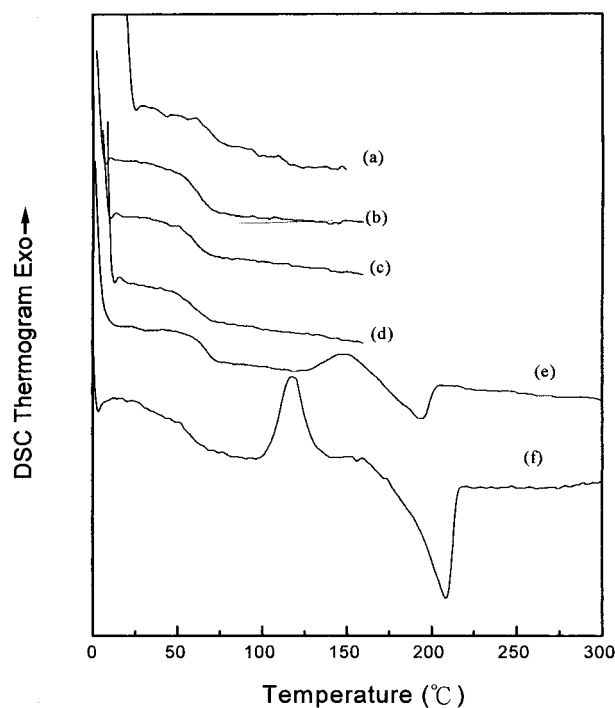**Figure 1** The DSC thermogram curves of nylon 6/novolac type phenolic resin blends with various compositions (wt %) of (a) 0/100, (b) 10/90, (c) 20/80, (d) 40/60, (e) 70/30, and (f) 90/10.
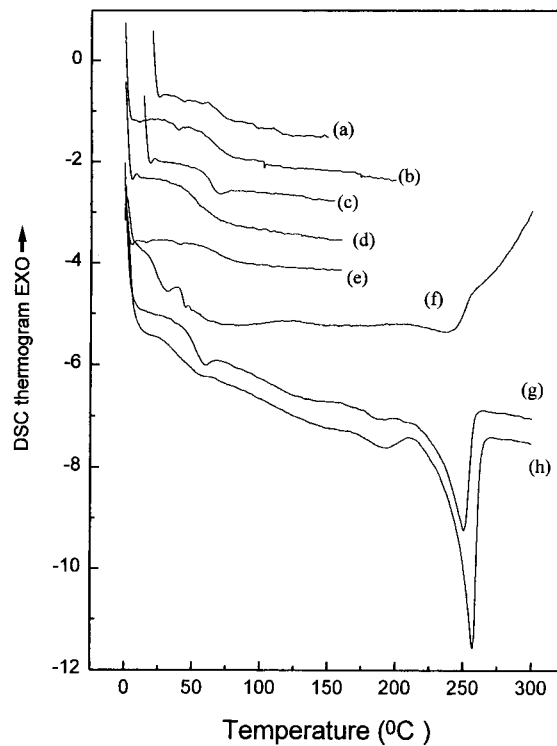

Figure 2 The DSC thermogram curves of nylon 66/novolac type phenolic resin blends with various compositions (wt %) of (a) 0/100, (b) 10/20, (c) 25/75, (d) 30/70, (e) 40/60, (f) 55/45, (g) 70/30, and (h) 90/10.

Table II   Parameters in Gordon–Taylor[11] and Kwei[9] Equations

Material	T_g (°C)	ρ at 25°C (g/mL)[a]	$\Delta\alpha \times 10^3$ (°C)	k Value
Novolac	69.86	1.2575	1.646	—
Nylon-6	43.94	1.008	2.617	0.5042
Nylon-66	46.05	1.028	2.497	0.5389

[a] The density was measured with a pycnometer.

scribed in previous reports.[7,15] The materials used are summarized in Table I.

Nylon 6 was obtained from the Taiwan Chemical Co. (Taiwan), and nylon 66 was received from DuPont.

Sample Preparation

The preparation of DSC specimen was as follows: the phenolic/polyamide blend was prepared by mixing the blend in phenol at room temperature according to the designed composition. The mixed solution
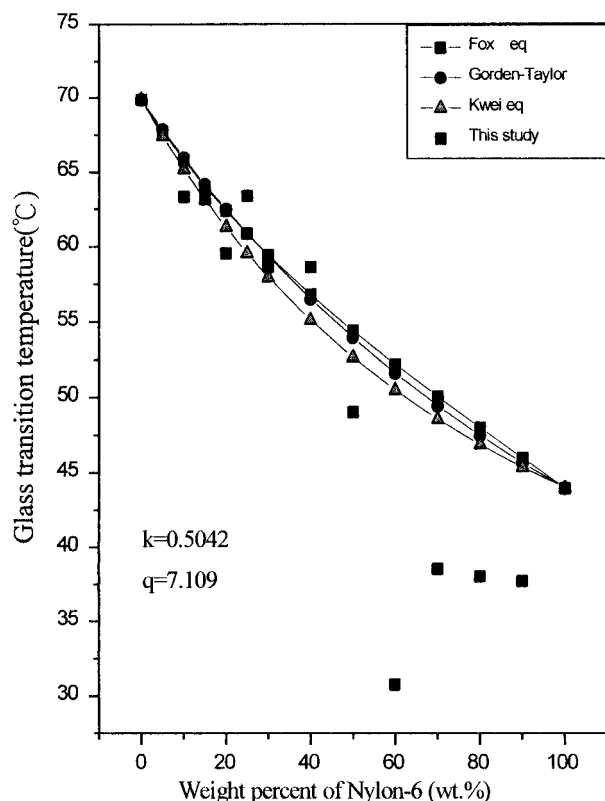

Figure 3   Experimental and theoretical predictions of T_g vs. the composition of nylon 6/novolac type phenolic resin blends.
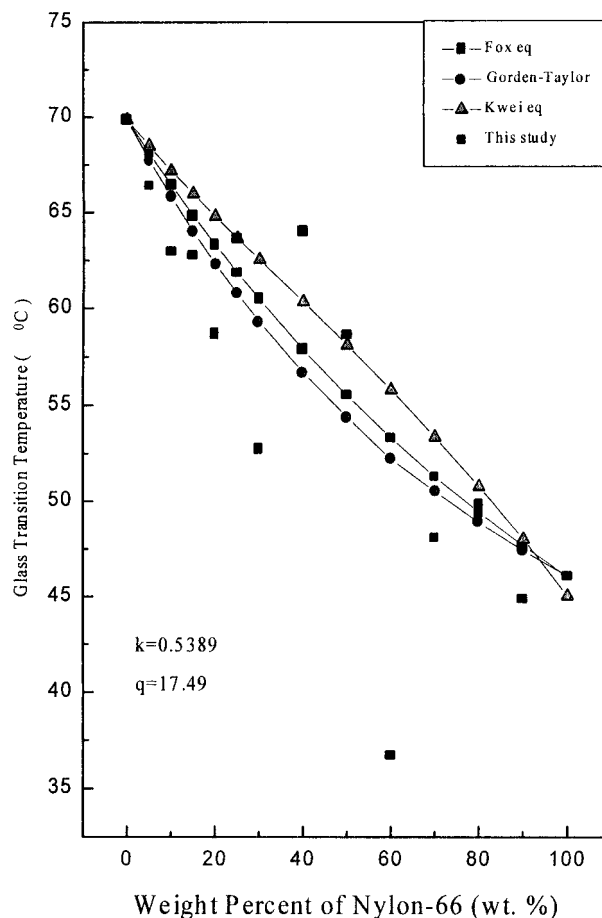

Figure 4   Experimental and theoretical predictions of T_g vs. the composition of nylon 66/novolac type phenolic resin blends.

was stirred for 3–5 min, and phenol was evaporated slowly at 80°C for 30 h. Then the blend was dried at 130°C for 1 day under a vacuum.

The IR specimens were prepared by the pulverizing DSC samples.

Property Measurements

The glass transition temperatures were determined by DSC (DuPont, DSC model 2900). The heating rate was 10°/min and the temperature range was 0–300°C. The measurements were made with 3–4 mg samples on the DSC sample plate after the specimens were quickly cooled to room temperature following the first scan. This procedure was adopted to ensure complete mixing of the polymer blend that completely removes the residual solvent and water in the specimen. The T_g values were determined at the midpoint of the transition point of the heat capacity (C_p) change. The reproducibility of the T_g values was estimated to be within ±1°C.

Table III   Comparison of q and k Values for Nylon 6/Novolac and Nylon 66/Novolac Blends

Parameter	Nylon 6/Novolac	Nylon 66/Novolac
k	0.5042	0.5389
q	7.109	17.49

RESULTS AND DISCUSSION

Glass Transition Temperature of Phenolic/Polyamide Blend

Figure 1 shows the DSC curves of phenolic resin blended with various nylon 6 contents. Figure 2 shows the resin blended with various nylon 6.6 contents. The glass transition temperatures were 68 ± 1, 46 ± 1, and $46.1 \pm 1°C$ for pure novolac type phenolic resin, nylon 6, and nylon 6.6, respectively. After quenching from the molten state, the rescanning results of samples show a single
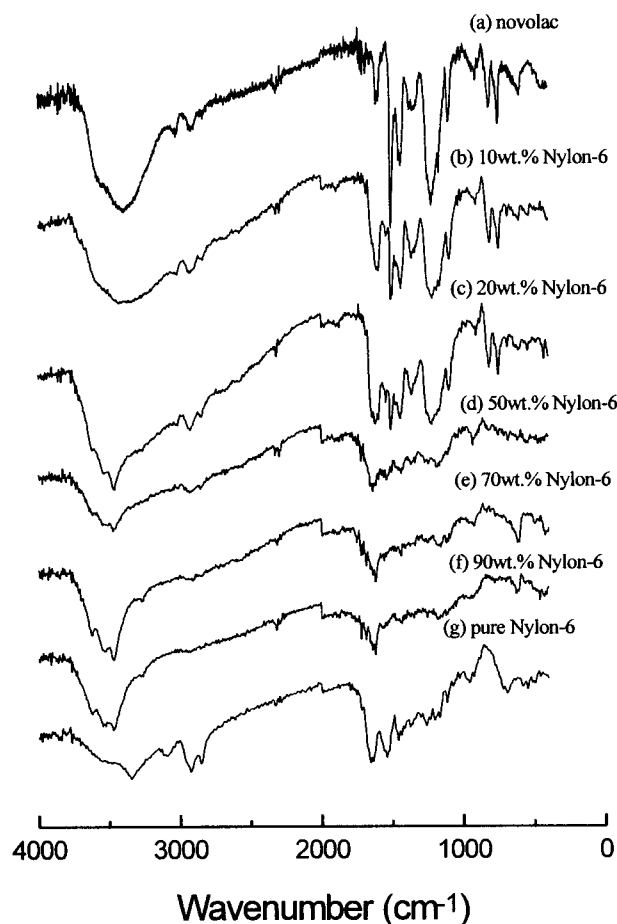

Figure 5   The IR spectra of nylon 6/novolac type phenolic resin blends with various compositions (wt %).
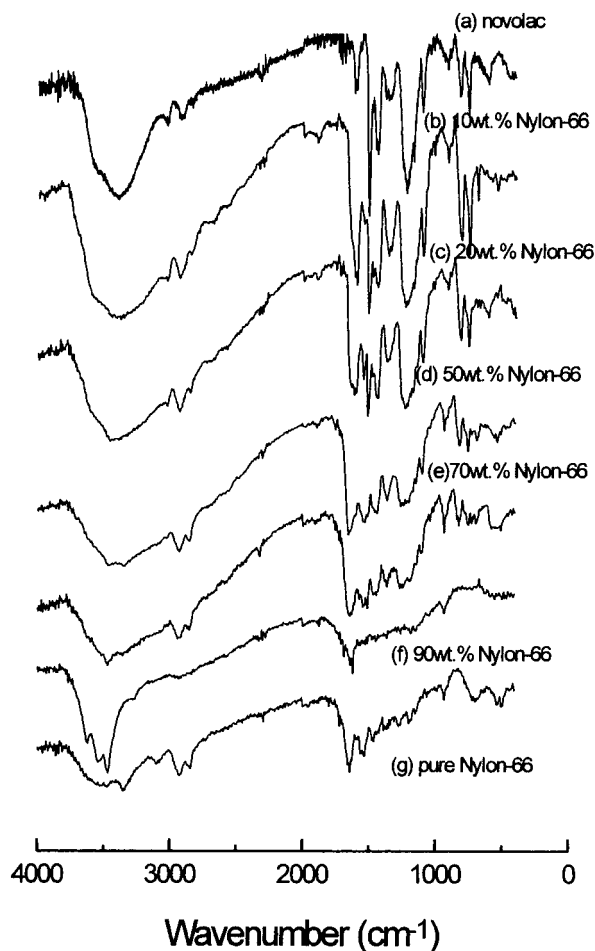

Figure 6   The IR spectra of nylon 66/novolac type phenolic resin blends with various compositions (wt %).

T_g throughout the whole blend range at various compositions of phenolic blends. This phenomenon suggests that the phenolic/polyamide blend system is miscible. The phenolic resin shows an unusually high T_g compared to other similar low molecular weight polymers because of the high density of intramolecular hydrogen bonding. Polyamide is a highly crystalline polymer, while phenolic resin is completely amorphous and relatively rigid. A characteristic of the polyamide is that it has high density of amide groups and a simple molecular structure. The flexible polyamide chain intersects into the free volume of the phenolic resin matrix and provides more opportunity to form hydrogen bonding, thus increasing the average strength of the hydrogen bonding.

In the phenolic resin poor region, the hydrogen bonding of the blend may decrease with polyamide content and the hydrogen bonding no longer plays a key role in affecting the molecular motion of the phenolic/polyamide blend. An endo-
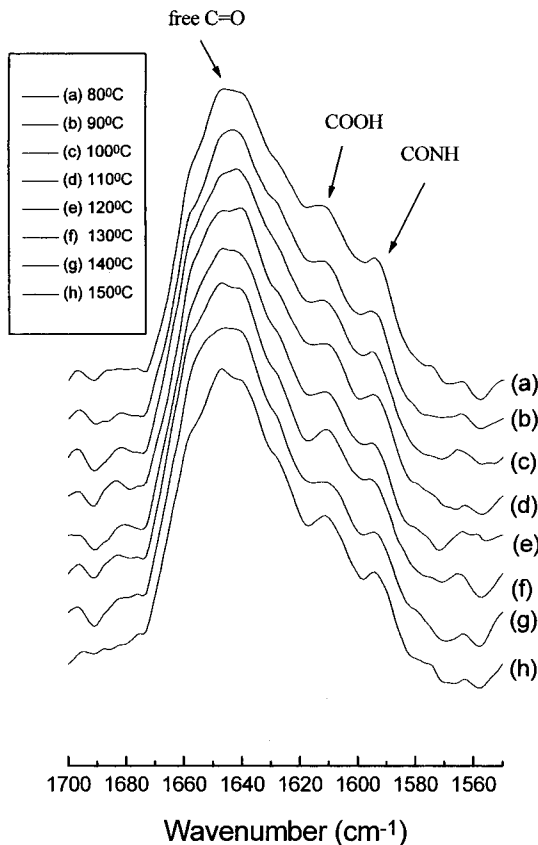
Figure 7 The IR spectra measured in the range of 80–150°C for the nylon 6/novolac (30/70) blend.

thermic peak in the DSC curve can be seen when polyamide content exceeds 60 wt % nylon 6 and 50 wt % nylon 66 in these blend systems. The hydrogen bonding is gradually replaced by dispersion force (randomly) in the phenolic resin poor region. The crystalline phase of polyamide is exhibited in the DSC curve for the phenolic resin poor region because the phenolic resin cannot provide enough hydroxyl groups to destroy the crystalline lattice of the polyamide.

Intermolecular Hydrogen Bonding of Phenolic/ Polyamide Blend

In this study the fit of the T_g from DSC by the Kwei, Gordon–Taylor, and Fox equations[9–12] was investigated. The intermolecular hydrogen bonding of the blending of novolac type phenolic resin with polyamide is explained. The Fox equation is

$$\frac{1}{T_{gb}} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \tag{1}$$

The Gordon–Taylor equation is

$$T_{gb} = \frac{\omega_1 T_{g1} + k\,\omega_2 T_{g2}}{\omega_1 + k\,\omega_2} \tag{2}$$

$$k = \frac{\rho_1 \Delta\alpha_2}{\rho_2 \Delta\alpha_1} \tag{3}$$

where the T_{gi} is the glass transition temperature of polymer i, ω_i is the weight fraction of polymer i, ρ_i is the density of polymer i, and $\Delta\alpha_i$ is the coefficient of thermal expansion of polymer i.

All data fit the Gordon–Taylor equation as listed in Table II. Near the T_g we can use the Simha–Boyer model[15] to calculate the difference of the coefficient of thermal expansion between the glass state and the molten state. The Simha–Boyer model is
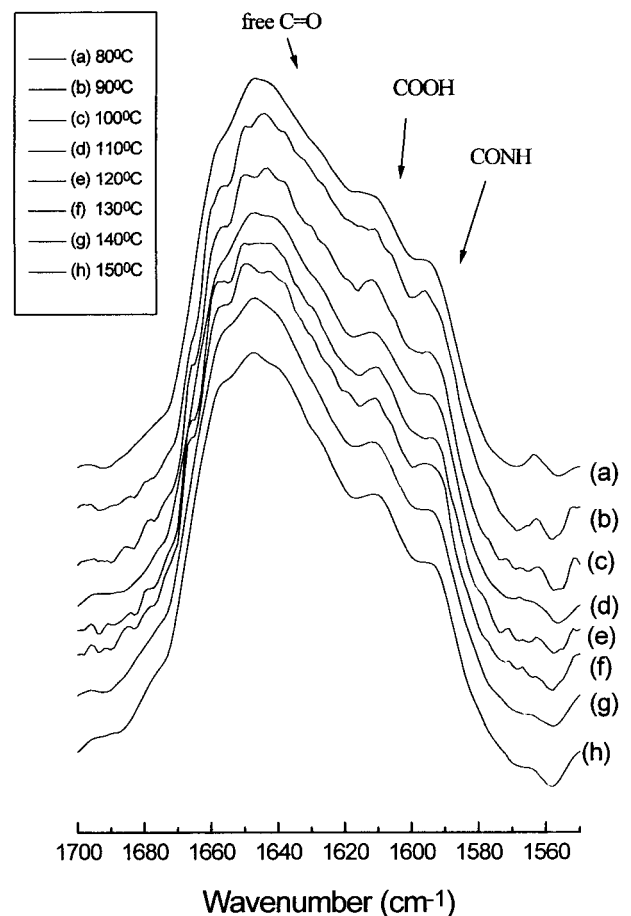
$$\Delta\alpha T_g = 0.115 \tag{4}$$

Figure 8 The IR spectra measured in the range of 80–150°C for the nylon 66/novolac (50/50) blend.
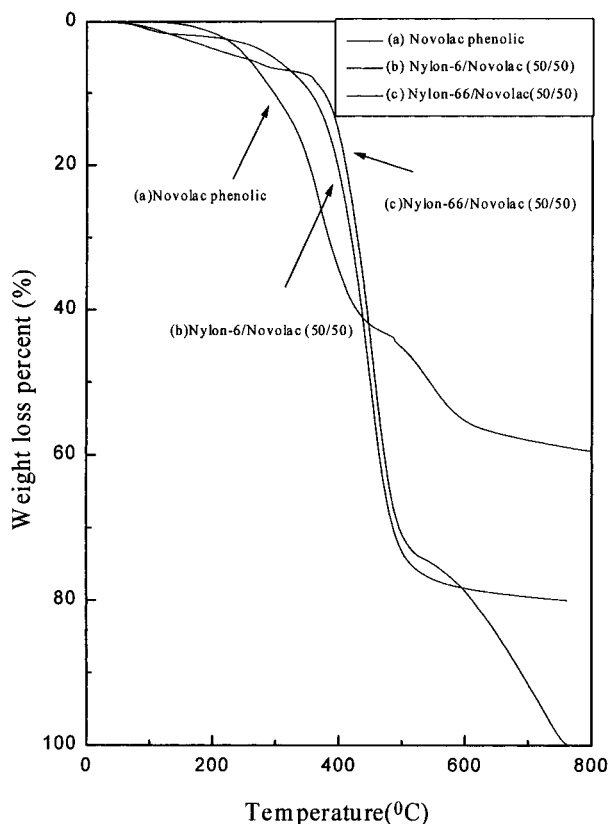
Figure 9 TGA curves of (a) neat novolac, (b) nylon 6/novolac (50/50), and (c) nylon 66/novolac (50/50) at a heating rate of 10°C/min in air.

The Kwei equation is

$$T_{gb} = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2} + q\omega_1\omega_2 \tag{5}$$

where q is the fit parameter of the intermocular force. The q values were obtained from Figures 3 and 4.

From Figures 3 and 4 we find that when the nylon 6 content of the blending is greater than 40 wt % and the nylon 66 content is greater than 20 wt %, the experiment data deviate from the Yang et al. equation; this situation is caused by the phenolic resin poor region of the blend. Hydrogen bonding of the molecular motion is not the only important parameter; the London dispersion force is another parameter that must be considered. For the nylon 6/novolac system the interaction of the crystallizable chemical potential of nylon 6 is an important force. In the phenolic resin poor region of the blend, the O—H functional group content of phenolic resin is not high enough to react well with the amide functionality of nylon 6. Hence, self-hydrogen bonding of nylon 6 is the primary force. When enough nylon 6 is added, the effect of London dispersion forces is stronger than the effect of intermolecular hydrogen bonding. In the phenolic resin poor region of the blend, the effect of intermolecular hydrogen bonding on T_g is less significant.

The value of q is an intermolecular force. Table III shows that the intermolecular force of the nylon 66/phenolic resin ($q = 17.49$) is higher than that of the nylon 6/phenolic resin ($q = 7.109$).

IR Spectra of Phenolic/Polyamide

Figures 5 and 6 show the hydrogen bonding in the O—H group in the IR absorption spectra with various polyamide contents. Figure 5 shows that $2800-3200$ cm^{-1} is the C—H group absorption that is decreased with increased novolac phenolic resin, and 1600 cm^{-1} is the C$_6$H$_6$ group absorption that increased with decreased novolac phenolic resin. The $3700-3000$ cm^{-1} is the O—H group absorption and $3500-3400$ cm^{-1} is the N—H group absorption. The 3591 cm^{-1} absorp-

Table IV   Curve-Fitting Results of ν, $\bar{\omega}_{1/2}$, and Af of Nylon 6/Phenolic Resin 70/30 (w/w) Blends

Temp. (°C)	Free C=O			H Bonded		COOH	H Bonded		CONH	
	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	f_b
80	1647.5	25.16	645.65	1616.0	36.48	619.9	1592.5	7.59	33.7	0.4029
90	1647.4	24.88	622.3	1617.7	33.915	523.1	1593.4	8.25	38.1	0.3754
100	1647.6	25.53	663.79	1616.8	33.62	503.81	1593.1	8.44	34.176	0.3508
110	1647.7	26.41	723.01	1615	34.45	513.2	1592.1	7.63	29.87	0.3337
120	1647.7	25.52	685.66	1616.7	31.98	434.94	1593.5	8.20	31.09	0.3118
130	1647.7	29.74	877.17	1610.3	36.69	502.43	1592.8	5.64	11.483	0.2808
140	1647.4	31.32	960.14	1609.0	34.81	460.61	1591.5	5.97	14.02	0.2479
150	1646.0	33.32	1008	1606.8	31.4	394.71	1591.3	5.51	14.93	0.2132

Table V   Curve-Fitting Results of ν, $\bar{\omega}_{1/2}$, and Af of Nylon-66/Phenolic Resin 50/50 (w/w) Blends

Temp. (°C)	Free C=O			H Bonded		COOH	H Bonded		CONH	
	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	ν (cm^{-1})	$\bar{\omega}_{1/2}$ (cm^{-1})	Af (%)	f_b
80	1650.0	26.88	1417.5	1617.1	35.23	1475.3	1592.6	13.01	174.98	0.4370
90	1648.3	30.943	1810.7	1612	37.04	1618.3	1591.6	9.99	104.67	0.3881
100	1648.9	29.2	1679.2	1613.7	34.64	1451	1591.9	10.41	131.2	0.3858
110	1649.3	28.92	1635.7	1614.3	34.55	1371.3	1592.1	11.96	154.25	0.3834
120	1649.3	30.99	1850.5	1611.5	36.97	1482.8	1591.5	8.36	74.43	0.3594
130	1648.6	34.14	2142.5	1609	35.87	1361.5	1591.7	7.42	69.41	0.3081
140	1648.6	33.852	2170.7	1608.7	34.63	1289.7	1591	8.76	69.58	0.2945
150	1648.4	36.2	2365.3	1606.9	35.282	1304	1591.1	7.3416	51.4	0.2764

tion is the free O—H peak that decreases with increased polyamide, and at 3450 and 3250 cm^{-1} the hydrogen bonding is caused by a broad O—H group region that is increased with decreased polyamide.

In the phenolic/polyamide blends we found that hydrogen bonding in the amide group of the polyamide reacted with the hydroxyl group of the phenolic resin. The intramolecular hydrogen bonding (CONH) and intermolecular hydrogen bonding (COOH) can be determined by IR absorption in 1500–1700 cm^{-1}. Figures 6 and 7 confirm that COOH and CONH peaks are decreased with an increase of temperature, while the "free" hydrogen bonding is increased with an increase of temperature.

From Tables IV and V one can find that the hydrogen bonded CONH and COOH of the nylon 66/novolac type phenolic blend are larger than those of the nylon 6/novolac type phenolic blend. Hence, it may be concluded that the hydrogen bonding of the nylon 66/novolac type phenolic blend is larger than that of the nylon 6/novolac type phenolic blend. These results coincide with the values of k and q. From Tables IV and V one can find that the percentage of free C—O of the nylon 6/novolac type phenolic blend at high temperature is larger than that of the nylon 66/novolac type phenolic blend. Consequently, the decomposition temperature of the nylon 66/novolac type novolac blend is higher than that of the nylon 6/novolac type phenolic blend. The results agree with the TGA data.

CONCLUSIONS

1. The phenolic resin/polyamide blend is a competely miscible system in which the flexible amide chain of the polyamide backbone penetrates the rigid phenolic resin structure.
2. The IR spectra of the phenolic resin/polyamide blend confirm the existence of hydrogen bonding.
3. Hydrogen bonded CONH and COOH contents in the nylon 66/novolac blend are larger than those of the nylon 6/phenolic blend, and the percentage of free C—O for the polyamide/novolac blends increases with temperature.

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